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Memory Effects and Multistability in Alignment of Nematics at Surfaces with Inhomogeneous Random Anchoring

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Alignment mechanisms for nematics at a macroscopically isotropic polymer surface are studied in cells where the second surface provides strong anchoring. Surface morphology of tested surfaces was studied using Atomic Force Microscopy and Scanning Electron Microscopy. We observed in polarizing microscope that the temperature gradient across the cell during transition from isotropic to nematic state strongly affects the alignment at the tested surface. We present a model that explains the temperature gradient effect. The initial patterns formed at the tested surface recover after multiple phase transitions but they can be erased by the temperature exposure well above the nematic-isotropic transition.

Keywords: anchoring; memory effect; nematic liquid crystal; random surface

1. INTRODUCTION

The alignment of liquid crystals (LCs) at the boundary surfaces is important for both fundamental science and various technological applications. The mechanisms of the interaction between LC and the substrate surface are complex and are not fully understood yet. Recently significant efforts have been directed towards studies of the interfacial alignment mechanisms for various substrate surfaces. The strong surface treatment results in the predictable stable LC alignment. More intriguing cases are the surfaces which induce a

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weak, random or competing LC alignment that may exhibit multistability and memory effect in alignment. Irradiation with polarized light of substrates made of photosensitive polymers creates homogeneous anchoring (photoalignment) [1]. The photoalignment may be weak enough to be comparable with an initial random anchoring and can be compensated by irradiation with orthogonal polarization [2]. The competing LC alignment can be also created with rubbings in orthogonal directions. Such rubbings were produced at shared surface [3] or at micron-sized adjacent pixels [4,5]. The mutual alignment of LC and polymer was investigated for soft polymer surfaces when LC is able to modify the aligning properties of the substrate [6]. Long-term torque caused by elastic, electric and magnetic forces can also produce very slow polar [7] and azimuthal [8,9] rotation (gliding) of the easy axis.

The objective of the article is to study the alignment mechanisms for nematic LCs at a polymer surface without macroscopic anisotropy. The untreated polymer provides tangential (in-plane) alignment with random azimuthal orientation of polymer chains and morphological features. We investigate alignment of nematic LC sandwiched between a standard substrate with strong planar alignment and untreated surface of a hard polymer film. It was found that alignment on the untreated surface strongly depends on the sign of temperature gradient during LC cooling from the isotropic state. The model for the temperature gradient effect is proposed.

The article is organized as follows. Section 2 describes experimental method and cells preparation conditions. In Section 3 we present experimental results and their discussion. Section 4 describes proposed model and its analysis which allows us to understand why temperature gradient affects the alignment at the random surface. Finally, conclusions are included in Section 5.

2. EXPERIMENTAL

In our experiments the nematic liquid crystal, 5CB is sandwiched in combined cells with two different types of substrate surfaces: a reference surface and a random surface. The rubbed polyimide film on an indium tin oxide (ITO)-coated glass serves as a reference surface which provides a strong uniaxial anchoring. To create the random surface, fluorinated polyvinylcinnamate (PVCN-F) is spin-coated from 0.1% dichorlethane solution on ITO-covered surfaces and then baked for 30 min at 80°C to evaporate the solvent. To avoid polymer dissolving by liquid crystal the PVCN-F film was irradiated by non-polarized UV light.

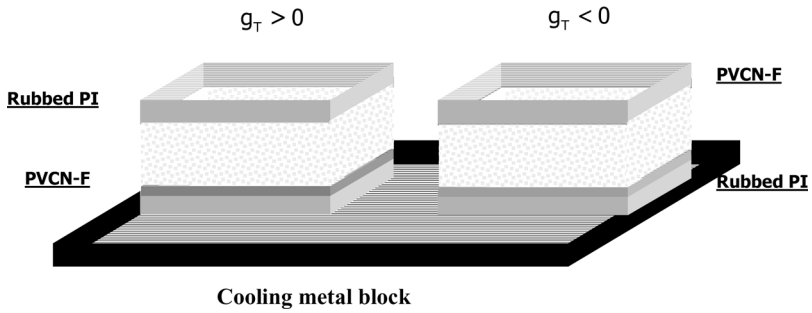


FIGURE 1 Schematic sketch of cooling the combined cells in the opposite temperature gradients: (a) $g_T > 0$ and (b) $g_T < 0$.

The morphology of the random surface is characterized using Scanning Electron Microscopy (6300 SEM, Jeol) and an Atomic Force Microscopy (AFN, Nanoscope III, Digital Instruments). The AFM surface images have been taken in tapping mode before and after UV irradiation of the substrates. Substrates were irradiated for 5 minutes by non-polarized UV light with wavelength of 365 nm and intensity of $6\,mW/cm^2$.

The empty cells are pre-heated to 50°C and filled with 5CB nematic in an isotropic phase. Cells are then cooled down on metal block in thermostat at 30°C in the temperature gradient g_T (defined in the direction from the random substrate to the rubbed reference substrate) formed due to the difference in heat conductivities of air and metal. Figure 1 shows two different cooling conditions for $g_T < 0$ and $g_T > 0$. This cooling method results in nematic phase nucleation either at the random surface or at the reference surface.

To study the director orientation at the random surface we place the cells between two polarizers and measure the transmittance of the system at room temperature. The input polarizer placed at the side of reference surface is oriented parallel to the rubbing direction. Cells are 50 microns thick which is enough to satisfy the Mauguin regime [10]; therefore the intensity of transmitted light is determined by the mutual orientation of analyzer and the director at the tested surface:

$$I_t = I_0 \cos^2(\alpha - \overline{\varphi}) \tag{1}$$

where α is the azimuthal angle of analyzer, φ is the azimuthal angle of the director at the tested surface. Rotation of analyzer allows one to reconstruct the distribution function of the director orientation at the tested surface [11].

To investigate the stability of the alignment at the random surface (a memory effect), cells were heated up to the isotropic phase, kept at the elevated temperature for certain time and then cooled down again into nematic phase under either the same or the opposite temperature gradient.

3. RESULTS AND DISCUSSION

3.1. Surface Characterization

The SEM image of the surface morphology for the PVCN-F films deposited with the conventional spin-coating method is shown in Figure 2. It is found that there are the multiple morphological features with different sizes and frequency on the tested random surfaces. These observations are also confirmed by the AFM tapping mode imaging of different scanned areas. Figure 3 shows the AFM images that reveal the complexity of the PVCN-F surface morphology. There are two distinct surface profiles with different peak heights.

The tested substrates were exposed to the non-polarized UV irradiation to cross-link the polymer in order to prevent possible polymer dissolving in the nematic liquid crystal. We used the non-polarized UV irradiation to keep the surface macroscopically isotropic, as the linearly polarized irradiation would provide photoalignment [12,13]. It appeared that the exposure to light intensity of $6\,mW/cm^2$

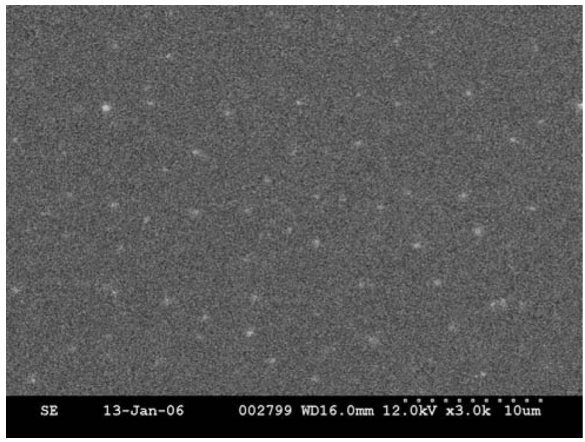
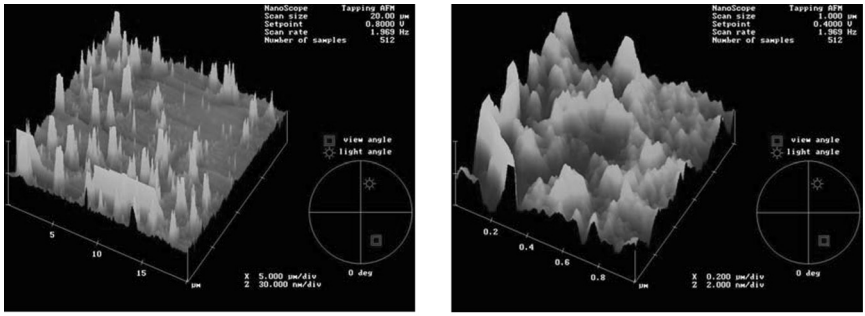


FIGURE 2 SEM image of the PVCN-F film. The scale bar represents 10 microns.



(a) (b)

FIGURE 3 AFM images of the PVCN-F film with different scanned areas: a) $20 \times 20\,\mu m^2$; and b) $1 \times 1\,\mu m^2$.

for 5 minutes slightly smoothes the surface profile of the films without inducing any macroscopic anisotropy.

3.2. LC Alignment

We observed that LC alignment at the random surface essentially depends on the direction of the temperature gradient during the first cooling from the isotropic phase. Figure 4 presents the photographs in parallel (a) and crossed (b) polarizers for a pair of identical cells cooled in opposite temperature gradients. In the case, when the nematic phase nucleates at the random surface ($g_T > 0$), the distribution of azimuthal alignment at the random substrate is practically isotropic. In the case, when the nematic phase nucleates at the reference surface ($g_T < 0$), it imposes the substantial anisotropy in the azimuthal alignment at the random surface. Thus there are two stable structures that can be formed in the cell during the first cooling: planar mono-domain undisturbed structure and poly-domain structure with random twists. The sign of the temperature gradient determines which one of these two structures will appear.

3.3. Alignment Memory Effect

To study the stability of the director alignment at the random surface a pair of identical cells was prepared. Both cells were cooled down from the rubbed surface ($g_T < 0$) to create uniform mono-domain structures (Fig. 5a). Then cells were reheated above the clearing point temperature ($T_{NI} = 35^\circ C$) and kept for an hour at $50^\circ C$. After that one of the

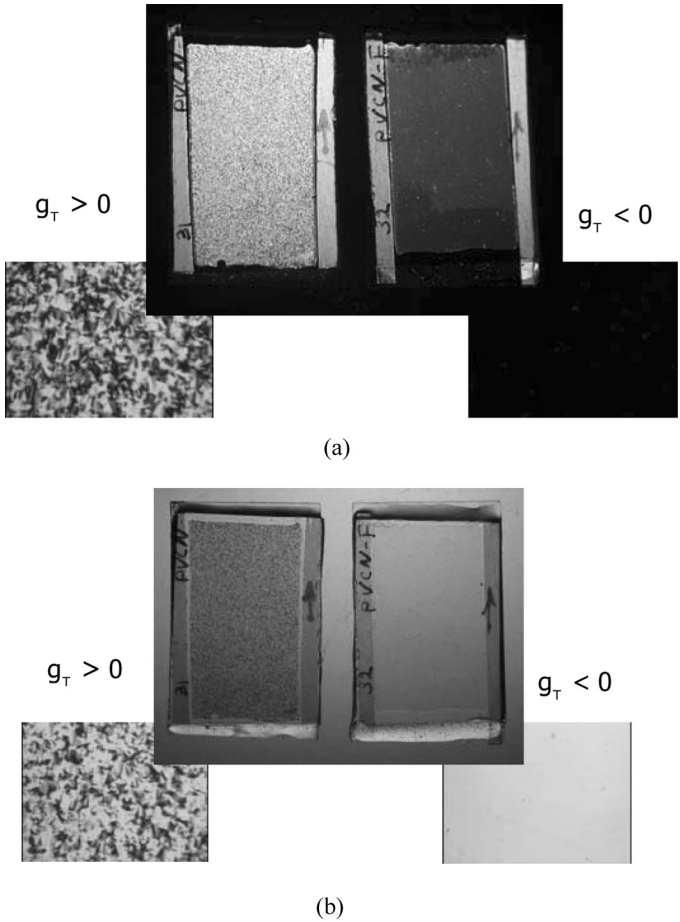


FIGURE 4 Photographs and microscope images of a pair of identical cells filled with 5CB. The pictures are taken after the first cooling from isotropic to nematic state in opposite temperature gradients: (a) between crossed polarizers, and (b) in parallel polarizers.

cells was cooled from the reference surface, and the other was cooled from the random surface. Despite the opposite temperature gradients during the second cooling, both cells revealed undisturbed mono-domain structure (Fig. 5b), exhibiting the alignment memory effect.

The experiment was then repeated for the same cells with the uniform mono-domain structure (Fig. 6a). This time the cells were reheated up to 70°C and kept for one hour at that temperature. It appeared that in this case the cell forgot the alignment induced during

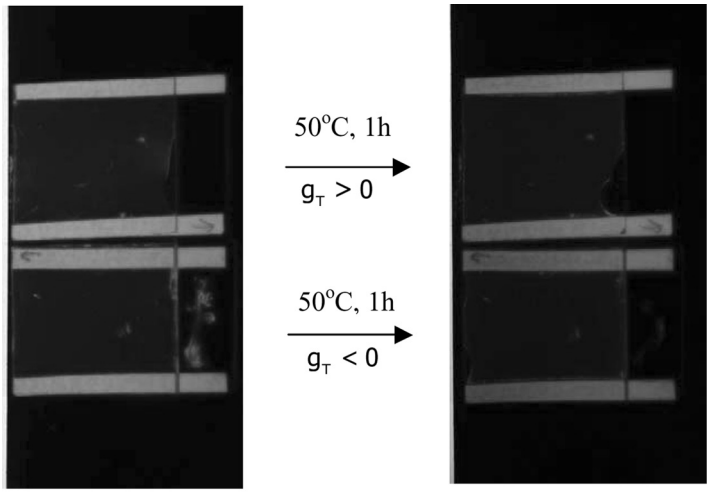


FIGURE 5 (a) Photographs of a pair of identical cells filled with 5CB. (b) When the cells are heated slightly above the clearing point (50°C) and kept at that temperature for an hour and then cooled in the opposite temperature gradients, the initial patterns recover in both cells showing the memory effect.

the first cooling and acquired the alignment according to the conditions of the last cooling (Fig. 6b). Therefore one can assume that exposure for one hour at 70°C erases the memory of previous cooling cycles.

4. MODEL

To explain the observed temperature gradient effect, we assume that alignment at the random surface of rigid polymers emerges as a result of ordering of adsorbed LC molecules into surface domains during I-N phase transition. Therefore, if (1) $g_T < 0$ the domains are formed when reference substrate already imposed mono-domain structure in the bulk; if (2) $g_T > 0$, the surface domains are formed at the random substrate while reference substrate is screened by a layer of isotropic phase and does not affect director orientation.

To develop a quantitative model we start with elastic Frank-Oseen energy:

$$F_{FO} = \int dV \frac{1}{2}(K_{11}(\operatorname{div}\mathbf{n})^2 + K_{22}(\mathbf{n}\cdot\operatorname{rot}\mathbf{n})^2 + K_{33}[\mathbf{n}\times\operatorname{rot}\mathbf{n}]^2) \quad (2)$$

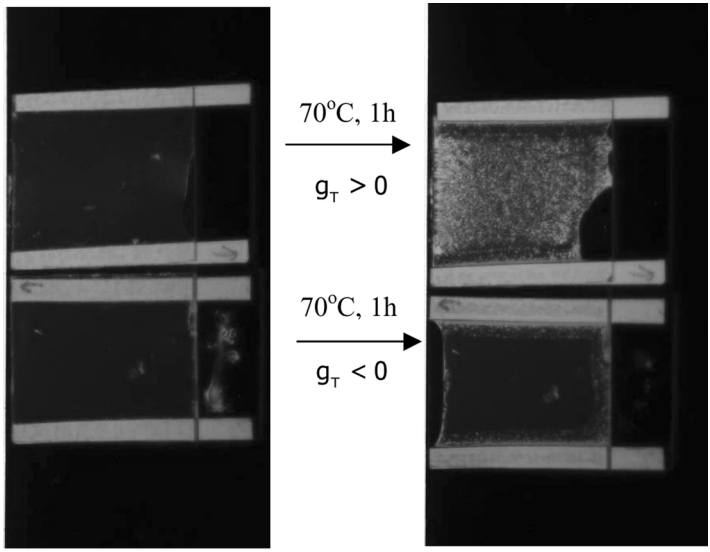


FIGURE 6 (a) Photographs of a pair of identical cells filled with 5CB. (b) When the cells are heated far above the clearing point (70°C) and kept at that temperature for an hour and then cooled in the opposite temperature gradients, new patterns appear that reflect the last temperature gradient demonstrating the memory erase.

In the nematic cell with tangential anchoring the director remains in Oxy plane $\mathbf{n} = (\cos\varphi, \sin\varphi, 0)$. In the two-bulk-constant approximation, $K_{11} = K_{33} = K$ we obtain

$$\mathrm{F_{FO}} = \int \mathrm{dV}\left\{\frac{\mathrm{K}}{2}\left(\left(\frac{\partial\varphi}{\partial x}\right)^2 + \left(\frac{\partial\varphi}{\partial y}\right)^2\right) + \frac{\mathrm{K_{22}}}{2}\left(\frac{\partial\varphi}{\partial z}\right)^2\right\} \tag{3}$$

Minimization $\delta\mathrm{F_{FO}} = 0$ results in the Euler-Lagrange equation:

$$K\left(\frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2}\right) + \mathrm{K_{22}}\frac{\partial^2\varphi}{\partial z^2} = 0. \tag{4}$$

The finite solution of Eq. (4) can be presented as the Fourier series:

$$\varphi = \sum_{\mathbf{q}}[a_{\mathbf{q}}^{+}\exp(tqz) + a_{\mathbf{q}}^{-}\exp(-tqz)]\exp(i\mathbf{q}\boldsymbol{\rho}) \tag{5}$$

where $\boldsymbol{\rho} = \{x, y\}$, $\mathbf{q} = \{q_x, q_y\}$, $q = |\mathbf{q}|$, $t = \sqrt{K/K_{22}}$.

We consider two cases of the boundary conditions, that correspond to opposite signs of the temperature gradients during cooling process: (1) if the entire cell is in the nematic phase, then the strong anchoring at the reference substrate ($z = d$) provides the condition $\varphi(d) = 0$; (2) if the nematic phase and the reference substrate are separated by the layer of the isotropic phase, then the condition $(d\varphi(z = b)/dz) = 0$ is satisfied at the nematic-isotropic interface ($z = b$). Taking into account the boundary conditions Eq. (5) reads:

$$\varphi = \sum_{\mathbf{q}} \varphi_{\mathbf{q}} U_{(m)}(z) \exp(i\mathbf{q}\boldsymbol{\rho}), \tag{6}$$

where $U_{(1)}(z) = \sinh[tq(d-z)]/\sinh[tqd]$, $U_{(2)}(z) = \cosh[tq(d-z)]/\cosh[tqd]$. The denominators in $U_{(m)}(z)$ have been chosen to obey the condition $U_{(m)}(0) = 1$, thus $\varphi_{\mathbf{q}}$ are the Fourier harmonics of $\overline{\varphi}$ at the random substrate ($z = 0$).

Substituting (6) in (3) and integrating, we obtain:

$$F_{FO}^{(m)} = \frac{S}{2} \sum_{\mathbf{q}} \varphi_{\mathbf{q}} \varphi_{-\mathbf{q}} G_{(m)}(q) \tag{7}$$

where $G_{(1)}(q) = Kq \coth(tqd)/t$, $G_{(2)}(q) = Kq \tanh(tqb)/t$, S is the substrate area.

To analyze the effect of the bulk elasticity on surface alignment we assume the parabolic azimuthal anchoring at the untreated surface with a constant anchoring coefficient W (the difference between the parabolic and Rapini-Papoular anchoring potentials [14] is negligible if W is large in comparison with the surface density of elastic twist energy $\sim K_{22}/d$):

$$\mathrm{F_S} = \int \frac{\mathrm{W}}{2} (\overline{\varphi} - \psi(\boldsymbol{\rho}))^2 \mathrm{dS} \tag{8}$$

Expanding angle $\psi(\rho)$ that defines the local easy axis orientation in Fourier series:

$$\psi(\boldsymbol{\rho}) = \sum_{\mathbf{q}} \psi_{\mathbf{q}} \exp(i\mathbf{q}\boldsymbol{\rho}) \tag{9}$$

one can obtain

$$F_S = \frac{WS}{2} \sum_{\mathbf{q}} (\varphi_{\mathbf{q}} \varphi_{-\mathbf{q}} - 2\varphi_{\mathbf{q}} \psi_{-\mathbf{q}} + \psi_{\mathbf{q}} \psi_{-\mathbf{q}}) \tag{10}$$

The equilibrium director field corresponds to the minimum of $F_{(m)} = F_S + F_{FO}^{(m)}$ with respect to $\varphi_{-\mathbf{q}}$, The minimum is achieved if

$$\varphi_{\mathbf{q}} = \psi_{\mathbf{q}} \frac{W}{W + G_{(m)}(q)} \tag{11}$$

and is equal to

$$F_{(m)} = \frac{S}{2} \sum_{\mathbf{q}} \frac{W G_{(m)}(q)}{W + G_{(m)}(q)} |\psi_{\mathbf{q}}|^2. \tag{12}$$

The temperature gradient effect can be interpreted with Eq. (11), where $G_{(1)}(q)$ and $G_{(2)}(q)$ correspond to the negative and positive signs of the gradient, respectively. Figure 7 shows that $G_{(1)}(q) > G_{(2)}(q)$. One can also obtain that $G_{(1)}(q) > K_{22}/d$, and $G_{(2)}(q) = Kbq^2$ for small q. Thus, one can conclude from Eq. (11) that, $G_{(1)}(q)$ can substantially suppress the director orientation at the random surface, $|\varphi_{\mathbf{q}}| < |\psi_{\mathbf{q}}|$, whereas for small q, $G_{(2)}(q)$ is negligible and the director orientation replicates the randomness of the tested surface, $\varphi_{\mathbf{q}} \approx \psi_{\mathbf{q}}$.

We assumed that W remains constant for all local inhomogeneities of the polymer surface. If we consider the polymer surface as a set of randomly oriented domains, then according to [15] $W(q) \propto q$. This fact, however, does not change the influence of $G_{(1)}(q)$ and $G_{(2)}(q)$ on the

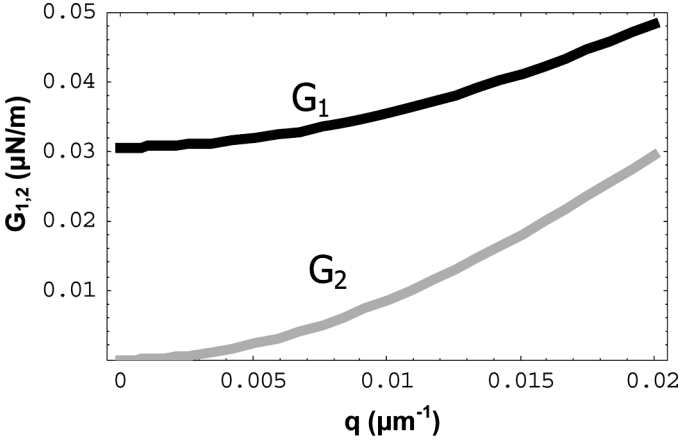


FIGURE 7 Functions $G_{(1)}(q)$ and $G_{(2)}(q)$, that control the director orientation at the tested surface, Eq. (11), after the cooling with negative and positive temperature gradients.

director orientation at the random surface and our explanation of the temperature gradient effect.

5. CONCLUSIONS

We observed that LC alignment at the random surface strongly depends on the direction of the temperature gradient during the first cooling from the isotropic phase. In the case when the nematic LC phase nucleates at the random surface, the distribution of azimuthal alignment at the random substrate is practically isotropic. In the case, when the nematic phase nucleates at the reference surface, it imposes the substantial anisotropy in the azimuthal alignment at the random surface. Our model explains the temperature gradient effect on alignment of liquid crystals at random surface of rigid polymers as a result of ordering of adsorbed LC molecules into surface domains during the I-N phase transition. The domains of adsorbed LC molecules survive transition into the isotropic phase but they can be destroyed if the cell is kept in the isotropic phase at high enough temperature.

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